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CONSIDERATIONS IN THE KINETICS OF PHOSPHORUS AND SULFUR REMOVAL
FROM BASIC ELECTRIC-ARC FURNACE STEELS

TECHNICAL REPORT WAL TR 310.9/1

BY

EUGENE DeLUCA

and

JOHN ZOTOS

DATE OF ISSUE - MARCH 1962

OMS CODE 5010.11-842
MATERIALS FOR ARMY WEAPONS AND COMBAT MOBILITY
D/A PROJECT 593-32-007

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TITLE

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FROM BASIC ELECTRIC-ARC FURNACE STEELS

ABSTRACT

An analysis of metal and slag composition data gathered during the operation of a 6-1/2-ton basic electric-arc furnace is made for the purpose of quantitatively describing the refining processes of dephosphorization and desulfurization. A kinetic model is proposed, and the data is examined in light of the model; agreement with theory is shown. Relations are obtained correlating metal and slag composition with the rate of the refining processes. The results and their ramifications are discussed with reference to the proposed model, actual operating procedure, extrapolation, and optimum processing time.

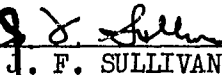


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INTRODUCTION

A complete description of the chemistry of steelmaking must necessarily include the kinetics of the refining processes. The term kinetics in the broadest sense must be interpreted to include, in the case of a heterogeneous reaction, rates of mass transfer to and from a phase boundary and rates of simultaneously occurring reactions at the phase interface. The general metal-slag reaction involves two immiscible liquid phases wherein a solute in phase A does not exist in the same form as in phase B. The reaction site is, therefore, confined to the phase boundary; and the reaction is described as one which involves the transfer of the reactants from the bulk phases to the metal-slag phase boundary, single or multiple reactions at the boundary, and transfer of the reaction products from the boundary into the bulk phases. Cases whereby the over-all process rate is controlled by the rate of a sufficiently slow step are, fortunately, of frequent occurrence and permit attention to be focused on either a single mass transfer step or a single boundary reaction.

The dephosphorization and desulfurization kinetics of carbon-saturated iron and steels in the molten state have been the topic of a number of laboratory and production-scale investigations.^{1,2,3} While laboratory investigations are fruitful both in testing hypotheses and in evolving mechanisms, there is no great certainty in extrapolating the quantitative results to production-scale facilities. This unfortunate consequence follows from the inability to relate the quantitative results of kinetic experiments on heterogeneous reactions to the geometry and convection patterns associated with the reaction vessel. Indeed, complete specification of the conditions of convection is, in general, impossible. Hence, analysis of production-scale data in light of existing theories and mechanisms would seem to be of value in establishing some actual production-scale quantitative results. This report is the result of such an analysis.

This paper is the refinement and outgrowth of a previous work,⁴ the essentials of which appear here.

THE KINETIC MODEL

The treatment presented herein follows closely that given in the literature.^{5,6}

Motion of a molecular species in a fluid phase is a consequence of two additive effects: diffusion of the species, and convection (free or forced) or macroscopic motion of the fluid phase. At a point P in a fluid phase the instantaneous rate of mass flux of a molecular species in the (s) direction and normal to a differential element of surface dA may be represented by the following equation:

$$f_i(s) = \left(-D_i \frac{\partial C_i}{\partial s} + u(s) C_i \right) dA, \quad \dots (1)$$

where s is distance, the positive sense of which corresponds to the positive (s) direction; D_i is the diffusion coefficient; C_i is the concentration; $u(s)$ is the component of the fluid velocity in the (s) direction; and i denotes species i . The first term of the right-hand member of Equation 1 accounts for diffusion of the species, the second term for motion of the phase. All quantities appearing in Equation 1 are evaluated at P . At points on the phase boundary Equation 1, with (s) taken as the direction normal to the boundary, reduces to

$$f_i(n) = -D_i \frac{\partial C_i}{\partial n} dA \quad (n=0), \quad \dots (2)$$

inasmuch as the velocity component of the fluid normal to the phase boundary must vanish at points on the boundary. The (n) is used to emphasize direction normal to the phase boundary.

Consider a region R in space bounded by a closed surface S . A portion of the surface S is a plane surface A , and $\left(\frac{\partial C_i}{\partial n} \right)_{n=0} = 0$ over all S except A . The direction (n) then has the same sense at all points on A ; the positive (n) direction is taken inward from the surface A . Species i is continually lost from R through A during the period of observation. The effective boundary layer thickness for species i is defined as

$$\delta_i = \frac{C_i^B - C_i}{\left(\frac{\partial C_i}{\partial n} \right)_{n=0}}, \quad \dots (3)$$

with all quantities save C_i^B evaluated at a general point on A . It is assumed that for $n > \epsilon$, $C_i(P, t) = f(t) = C_i^B$; that is, for $n > \epsilon$, C_i has no variation from point to point at fixed time t . Equivalently, appreciable concentration gradients are assumed to exist only in the vicinity of $A(n \leq \epsilon)$. The term C_i^B is referred to as the bulk phase concentration of i . Combination of Equations 2 and 3 yields

$$f_i(n) = -D_i \frac{(C_i^B - C_i)}{\delta_i} dA. \quad \dots (4)$$

The total rate of mass flux of species i through S is then obtained by integration of Equation 4 over A .

Consider now a metal-slag refining process involving the removal of species i from the metal phase by the sequence of steps previously described as involved in the general metal-slag reaction. Let R be identified with a volume of metal in contact with a volume of slag at the plane surface A . Application of the development leading to Equation 4 rests on the assumption of transport control. The assumption of transport control or, equivalently, postulation of chemical equilibrium at the metal-slag phase boundary is in keeping with the electrochemical nature or "nonmolecularity" of metal-slag phase boundary reactions and with the high temperature associated with the process. If it is further assumed that the over-all rate of the refining process is controlled by transport of the species from the bulk metal to the phase boundary, then for a differential element of interface area the instantaneous rate of mass flux of species i from the metal to the slag may be written, according to Equation 4, as

$$F_i = \frac{D_i}{\delta_i} (C_i^B - C_i^I), \quad \dots (5)$$

where, again, D_i is the diffusion coefficient in the metal, δ_i is the effective boundary layer thickness, C_i^B is the bulk metal molar concentration, C_i^I is the interface molar concentration, and i denotes species i . Conditions which support the above assumption include: (1) the bulk concentration of i in the metal \ll the bulk concentration(s) of the reaction product(s) in the slag; (2) the diffusion coefficient of i in the metal \ll the diffusion coefficient(s) of the reaction product(s) in the slag; and (3) the degree of turbulence in the metal \ll the degree of turbulence in the slag. Proceeding under this assumption and neglecting variation in the term $(D_i/\delta_i)(C_i^B - C_i^I)$ with position on A or, more precisely, taking $\left(\frac{\partial C_i}{\partial n}\right)_{n=0}$ as independent of position on A , the total instantaneous rate of mass flux from R is then given by

$$\int_A F_i dA = \frac{D_i A}{\delta_i} (C_i^B - C_i^I), \quad \dots (6)$$

where integration is over the area A of the metal-slag phase boundary. From a material balance on species i there follows

$$-\frac{D_i A}{\delta_i} (C_i^B - C_i^I) = \frac{d(V C_i^B)}{dt} = (V) \frac{dC_i^B}{dt}, \quad \dots (7)$$

or

$$-\frac{dC_i^B}{dt} = \frac{D_i A}{\delta_i V} (C_i^B - C_i^I), \quad \dots (8)$$

where t denotes time measured from the start of the observation period and V , the volume of the metal, is taken as constant. If it is assumed that C_i^I is small in comparison with C_i^B and that variation in $D_i A / \delta_i V$ with time is negligible, then

$$-\frac{dC_i^B}{dt} = a_i C_i^B, \quad \dots (9)$$

where

$$a_i \equiv \frac{D_i A}{\delta_i V}, \quad \dots (10)$$

and is constant. The requirement that $D_i A / \delta_i V$ will not vary with time is, in general, equivalent to the requirement that δ_i will not vary with time. It may be in order to remark here that in the case of forced convection, it is known that δ_i is independent of C_i^B and C_i^I . By definition, for a molecular species,

$$C_i^B = \frac{N_i}{V} = \frac{W_i}{V(MW)_i} = \frac{Y_i W_T}{V(MW)_i} = \frac{Z_i W_T}{100V(MW)_i}, \quad \dots (11)$$

where N denotes moles, W mass, MW molecular weight, Y mass fraction, and Z mass percent. The subscript T denotes total mass. For an atomic species mole numbers are replaced by atomic numbers and molecular weight by atomic weight. As a very close approximation

$$\frac{dC_i^B}{dt} = \frac{W_T}{100V(MW)_i} \frac{dZ_i}{dt}, \quad \dots (12)$$

and Equation 9 may be written as

$$-\frac{dZ_i}{dt} = a_i Z_i, \quad \dots (13)$$

from which there follows

$$- \log_{10} \frac{Z_i}{Z_{i0}} = \frac{a_i}{2.303} t, \quad \dots (14)$$

where Z_{i0} denotes mass percent of i at time zero. With the given assumptions, the species i transfer reaction, written schematically as



(the bar serving to indicate nonsimilarity of the molecular forms), may be said to be of "first-order" with respect to species i .

SOURCE OF DATA

Data obtained in recent metallurgical process investigations at the Watertown Arsenal Laboratories were analyzed to examine the significance of the proposed kinetic model for dephosphorization and desulfurization of basic electric-arc furnace steels under production-scale conditions. The assumptions made in arriving at the model, Equation 14, were considered appropriate for analysis of the refining processes. The process investigations were conducted for the purpose of developing an operating procedure for producing high quality, low sulfur, and low phosphorus steels in a 6-1/2-ton, basic electric-arc furnace. The melting practice, previously reported in detail,⁷ initially produced AISI 4140 steel and was later used to produce AISI steels 4330, high nickel 4325, 1040, and 4340. In addition to variations in the composition of the steel produced, systematic variations in the composition of the slags were introduced during the dephosphorization or oxidizing period and during the desulfurization or reducing period. At periodic time intervals during the dephosphorization and desulfurization periods, a sample of metal and slag was extracted from the respective bulk phase. The steel samples were quantitatively analyzed for elemental content (sulfur and phosphorus included) and the slag samples for silicon dioxide, iron oxide, calcium oxide, sulfur, and phosphorus content. Table I shows the metal and slag analyses obtained from the various steels at various intervals during the oxidizing period and the reducing period.

RESULTS, DISCUSSION, AND OBSERVATIONS

Application of the Model Equation

Notation is now introduced which will be used throughout the remainder of this report. The symbols $[i]$ and (i) are used to denote the instantaneous bulk weight percent of species i in the metal and slag phases, respectively. The subscript o refers to the start of an observation period in which time, t , is measured in minutes.

TABLE I

METAL AND SLAG ANALYSES*

HEAT	Steel	Operating Period	Time (min)	Metal Analysis								Slag Analysis					
				[C]	[Mn]	[Si]	[Cr]	[Mo]	[Ni]	[S]	[P]	(CoO)	(SiO ₂)	(FeO)	(S)	(P)	
A. AISI 4140	Oxidizing	0	0.450	0.290	0.020	0.050	- - -	- - -	- - -	0.024	0.022	33.92	17.62	13.80	0.076	0.082	
		20	0.390	0.260	0.010	0.080	- - -	- - -	- - -	0.026	0.008	36.52	18.04	11.00	0.083	0.083	
		80	0.050	0.070	0.060	0.040	- - -	- - -	- - -	0.028	0.004	32.36	17.55	29.70	0.060	0.150	
		150	0.030	- - -	0.050	- - -	- - -	- - -	- - -	0.025	0.001	26.00	7.35	48.30	0.095	0.041	
	Reducing	0	0.055	0.030	0.090	- - -	- - -	- - -	- - -	0.029	0.003	58.60	5.14	16.60	0.315	0.017	
		10	0.055	0.030	0.030	- - -	- - -	- - -	- - -	0.024	0.003	67.75	4.18	10.20	0.315	0.023	
		20	0.060	- - -	0.030	0.900	0.190	- - -	- - -	0.020	0.007	51.20	10.08	8.40	0.172	0.037	
		50	0.305	- - -	0.030	0.670	0.180	- - -	- - -	0.019	0.008	38.00	14.12	10.00	0.102	0.034	
		68	0.430	0.990	0.550	1.010	0.230	- - -	- - -	0.017	0.008	- - -	- - -	- - -	- - -	- - -	
B. AISI 4140	Oxidizing	0	0.475	0.280	0.030	0.040	- - -	- - -	- - -	0.020	0.012	44.74	17.92	12.30	0.143	0.081	
		30	0.415	0.380	0.050	0.080	- - -	- - -	- - -	0.024	0.008	40.92	18.84	10.80	0.083	0.081	
		95	0.020	0.110	0.010	0.020	- - -	- - -	- - -	0.027	0.005	28.74	20.72	32.40	0.033	0.124	
		145	0.030	- - -	- - -	- - -	- - -	- - -	- - -	0.032	0.003	20.48	11.96	50.70	0.092	0.085	
	Reducing	0	0.110	0.100	0.030	0.020	- - -	- - -	- - -	0.033	0.002	64.20	5.38	14.50	0.303	0.045	
		16	0.120	- - -	0.030	- - -	- - -	- - -	- - -	0.024	0.005	54.18	10.50	17.20	0.220	0.042	
		31	0.100	0.020	- - -	0.860	0.210	- - -	- - -	0.028	0.005	48.20	8.24	15.10	0.203	0.028	
		48	0.120	- - -	- - -	0.940	0.210	- - -	- - -	0.028	0.005	43.20	8.82	21.00	0.183	0.028	
		68	0.330	- - -	- - -	0.950	0.210	- - -	- - -	0.022	0.006	47.68	10.72	13.40	0.287	0.030	
		78	0.345	1.080	0.550	1.110	0.210	- - -	- - -	0.019	0.006	51.18	22.80	1.80	0.320	0.007	
C. AISI 4140	Oxidizing	0	0.600	0.540	0.040	1.280	0.290	- - -	- - -	0.025	0.009	33.50	19.70	10.55	0.082	0.052	
		20	0.540	0.510	- - -	1.330	0.290	- - -	- - -	0.021	0.008	38.50	20.80	7.72	0.118	0.067	
		80	0.100	0.270	0.030	0.860	0.260	- - -	- - -	0.022	0.007	30.80	20.80	11.20	0.037	0.048	
		115	0.060	0.190	- - -	0.890	0.310	- - -	- - -	0.016	0.006	38.40	11.30	20.20	0.153	0.157	
	Reducing	0	0.250	0.700	0.150	0.950	0.310	- - -	- - -	0.018	0.013	47.90	21.00	2.19	0.180	0.007	
		15	0.405	0.730	0.100	0.970	0.290	- - -	- - -	0.016	0.013	37.80	17.00	3.09	0.148	0.012	
		30	0.440	0.710	0.100	1.080	0.300	- - -	- - -	0.015	0.014	46.30	21.60	2.32	0.133	0.015	
		45	0.435	0.720	0.320	1.070	0.290	- - -	- - -	0.014	0.013	46.60	22.30	2.32	0.131	0.012	
		61	0.430	0.800	0.190	1.070	0.250	- - -	- - -	0.013	0.014	45.60	22.80	1.87	0.105	0.013	
D. AISI 4330	Oxidizing	0	0.250	0.510	0.080	0.950	0.380	2.03	- - -	0.028	0.008	37.10	18.00	15.87	0.131	0.130	
		20	0.445	0.480	0.050	0.370	0.420	2.01	- - -	0.026	0.007	38.90	15.20	13.64	0.150	0.140	
		80	0.130	0.080	0.030	0.070	0.380	2.18	- - -	0.024	0.004	25.20	18.00	21.80	0.048	0.139	
		120	0.065	0.070	0.040	0.180	0.370	2.12	- - -	0.025	0.002	38.40	13.80	23.10	0.140	0.087	
	Reducing	0	0.265	0.830	0.280	0.120	0.380	2.07	- - -	0.014	0.008	50.10	21.00	2.18	0.310	0.018	
		18	0.245	0.800	0.170	0.180	0.380	2.11	- - -	0.011	0.008	56.40	22.70	1.18	0.240	0.008	
		25	0.240	0.580	0.180	0.170	0.350	2.09	- - -	0.012	0.008	58.60	24.00	0.87	0.117	0.004	
		40	0.240	0.550	0.180	0.170	0.380	2.04	- - -	0.009	0.008	58.20	25.50	0.77	0.140	0.034	
		55	0.240	0.530	0.120	0.170	0.360	2.08	- - -	0.008	0.008	53.80	26.80	1.80	0.085	0.012	
		70	0.285	0.540	0.080	0.950	0.350	2.01	- - -	0.007	0.008	53.40	25.80	1.12	0.087	0.008	
104	0.280	0.960	0.230	0.960	0.370	2.04	- - -	0.005	0.007	44.50	29.30	2.44	0.044	0.007			
E. AISI 4330	Oxidizing	0	0.420	0.570	0.090	0.600	0.330	1.72	- - -	0.024	0.011	33.48	21.73	7.00	0.083	0.083	
		20	0.420	0.520	0.020	0.580	0.350	1.77	- - -	0.023	0.010	32.52	23.33	8.10	0.071	0.118	
		80	0.070	0.110	0.010	0.090	0.350	1.78	- - -	0.029	0.008	23.88	22.27	11.70	0.088	0.150	
		110	0.020	0.090	0.040	0.140	0.320	1.72	- - -	0.024	0.002	30.96	10.20	26.70	0.170	0.153	
	Reducing	0	0.210	0.510	0.130	0.230	0.310	1.67	- - -	0.018	0.005	48.16	19.15	2.00	0.290	0.021	
		15	0.200	0.480	0.120	0.520	0.380	2.06	- - -	0.015	0.006	42.48	21.25	1.90	0.230	0.021	
		30	0.200	0.470	0.110	0.880	0.370	2.02	- - -	0.017	0.006	38.24	21.87	2.80	0.120	0.027	
		45	0.310	0.440	0.080	0.880	0.380	2.07	- - -	0.014	0.006	39.24	20.74	3.50	0.120	0.024	
		60	0.305	0.420	0.060	0.850	0.370	2.08	- - -	0.014	0.006	46.75	20.10	4.30	0.054	0.038	
		75	0.310	0.390	0.080	0.850	0.370	2.07	- - -	0.014	0.005	35.40	20.85	4.40	0.048	0.042	
90	0.310	0.940	0.200	0.880	0.360	2.02	- - -	0.012	0.011	34.00	28.23	1.80	0.089	0.018			
F. AISI 4335	Oxidizing	0	0.405	0.600	0.140	0.600	0.450	2.28	- - -	0.023	0.009	40.80	20.42	9.20	0.071	0.069	
		20	0.410	0.590	0.010	0.540	0.410	2.36	- - -	0.023	0.008	39.44	21.06	7.80	0.083	0.080	
		80	0.060	0.130	0.040	0.250	0.440	2.44	- - -	0.023	0.006	26.40	20.54	18.70	0.048	0.074	
		115	0.050	0.080	0.050	0.140	0.410	2.38	- - -	0.020	0.005	35.44	6.18	33.30	0.186	0.096	
	Reducing	0	0.200	0.500	0.160	0.200	0.390	2.37	- - -	0.017	0.006	56.92	18.56	2.60	0.240	0.017	
		11	0.190	0.520	0.190	0.230	0.380	2.28	- - -	0.014	0.006	55.12	20.24	2.90	0.240	0.015	
		26	0.190	0.460	0.170	0.250	0.380	2.28	- - -	0.012	0.007	48.84	21.38	3.00	0.122	0.022	
		41	0.180	0.450	0.070	0.260	0.400	2.31	- - -	0.011	0.007	49.20	21.02	3.60	0.086	0.022	
		56	0.250	0.450	0.080	0.790	0.460	2.42	- - -	0.011	0.005	46.44	20.74	3.70	0.088	0.020	
		71	0.240	0.410	0.070	0.770	0.450	2.41	- - -	0.011	0.007	47.74	20.84	3.90	0.068	0.028	
86	0.235	0.400	0.120	0.770	0.460	2.43	- - -	0.011	0.008	38.26	21.44	6.10	0.026	0.038			
101	0.280	1.460	0.450	0.900	0.450	2.45	- - -	0.010	0.012	40.08	25.38	2.40	0.040	0.020			

TABLE I (CONT'D)
METAL AND SLAG ANALYSES*

HEAT	Steel	Operating Period	Time (min)	Metal Analysis							Slag Analysis						
				[C]	[Mn]	[Si]	[Cr]	[Mo]	[Ni]	[S]	[P]	(CaO)	(SiO ₂)	(FeO)	(S)	(P)	
G. AISI 4340		Oxidising	0	0.800	0.510	0.160	1.000	0.360	2.10	0.024	0.017	46.25	28.55	3.48	0.040	0.057	
			15	0.760	0.380	0.100	0.860	0.350	2.08	0.024	0.017	35.07	28.34	11.32	0.020	0.070	
			30	0.745	0.250	0.040	0.700	0.360	2.05	0.024	0.016	33.02	27.08	9.36	0.020	0.079	
			45	0.620	0.190	0.030	0.480	0.340	2.02	0.021	0.015	29.87	25.10	14.60	0.020	0.087	
			59	0.590	0.130	0.030	0.440	0.350	2.02	0.023	0.015	31.41	26.14	12.20	0.020	0.122	
			77	0.460	0.140	0.020	0.370	0.360	2.00	0.024	0.011	49.09	11.52	11.62	0.150	0.131	
			90	0.440	0.120	0.020	0.400	0.350	2.03	0.023	0.009	46.88	12.56	12.39	0.170	0.282	
			104	0.400	0.140	0.030	0.420	0.350	2.05	0.023	0.009	43.88	14.29	13.84	0.140	0.231	
		Reducing	0	0.370	0.470	0.230	0.440	0.350	2.01	0.021	0.010	42.33	15.43	10.26	0.120	0.067	
			20	0.380	0.470	0.140	0.480	0.340	2.00	0.019	0.012	36.06	15.78	5.79	0.115	0.068	
			44	0.380	0.830	1.340	0.490	0.340	1.97	0.013	0.012	41.28	17.03	6.11	0.285	0.078	
			59	0.370	0.810	1.330	0.520	0.340	1.97	0.010	0.011	42.59	17.66	3.34	0.280	0.078	
			74	0.370	0.820	1.270	0.490	0.340	1.95	0.008	0.012	43.40	18.84	3.21	0.200	0.076	
			84	0.380	0.830	1.580	0.550	0.330	1.96	0.006	0.013	40.03	17.82	5.13	0.170	0.070	
			101	0.370	0.820	1.510	0.770	0.330	1.99	0.005	0.012	42.18	19.81	2.87	0.140	0.061	
H. AISI 4340		Oxidising	0	0.540	0.430	0.050	0.560	0.220	1.18	0.018	0.008	41.80	19.70	11.40	0.057	0.096	
			15	0.420	0.420	0.030	0.560	0.230	1.18	0.019	0.008	33.80	18.80	10.40	0.047	0.070	
			30	0.500	0.340	0.030	0.450	0.220	1.18	0.020	0.007	34.40	21.00	14.30	0.048	0.096	
			45	0.400	0.200	0.040	0.290	0.210	1.18	0.020	0.007	34.90	22.70	17.50	0.029	0.118	
			60	0.270	0.150	0.020	0.200	0.220	1.21	0.019	0.007	29.80	21.80	18.20	0.028	0.087	
			75	0.180	0.140	0.030	0.160	0.210	1.18	0.019	0.007	30.20	23.60	17.30	0.029	0.118	
			90	0.110	0.120	0.060	0.170	0.210	1.18	0.019	0.007	30.40	25.10	9.70	0.022	0.098	
			105	0.070	0.120	0.030	0.150	0.220	1.18	0.022	0.005	40.30	15.50	24.20	0.098	0.140	
			120	0.050	0.100	0.030	0.180	0.220	1.19	0.022	0.004	52.40	17.80	10.40	0.130	0.044	
		Reducing	0	0.250	0.390	0.150	0.240	0.220	1.18	0.022	0.004	46.80	17.60	10.40	0.113	0.057	
			10	0.260	0.370	0.180	0.215	0.215	1.18	0.020	0.004	50.80	18.10	9.30	0.141	0.070	
			14	0.270	0.350	0.110	0.205	0.215	1.17	0.021	0.004	53.40	18.80	9.40	0.128	0.082	
			29	0.270	0.330	0.070	0.205	0.215	1.17	0.019	0.004	45.80	22.80	9.70	0.012	0.070	
			40	0.290	0.320	0.070	0.205	0.210	1.18	0.020	0.004	47.70	18.80	9.70	0.114	0.050	
			53	0.310	0.310	0.030	0.200	0.215	1.19	0.020	0.003	47.70	17.10	9.80	0.116	0.085	
	57	0.300	0.340	0.050	0.225	0.220	1.18	0.018	0.005	48.90	17.80	6.80	0.138	0.057			
	82	0.310	0.380	0.040	0.240	0.200	1.18	0.018	0.005	55.00	19.70	2.40	0.184	0.091			
	77	0.310	0.380	0.020	0.245	0.215	1.17	0.015	0.007	45.80	18.20	7.20	0.088	0.048			
	92	0.310	0.320	0.030	0.240	0.220	1.19	0.018	0.006	48.70	19.50	5.80	0.086	0.052			
	111	0.330	0.340	0.040	0.250	0.220	1.18	0.015	0.006	48.20	15.60	5.80	0.105	0.052			
	I. AISI 1040		Oxidising	0	0.440	0.280	0.080	0.010	- - -	- - -	0.024	0.011	53.88	16.70	11.50	0.182	0.058
				20	0.390	0.280	0.060	0.010	- - -	- - -	0.022	0.009	42.48	17.70	11.00	0.192	0.115
80				0.350	0.020	- - -	0.010	- - -	- - -	0.033	0.003	26.18	19.82	32.00	0.220	0.183	
135				0.350	- - -	0.010	0.010	- - -	- - -	0.029	0.001	29.60	5.04	45.80	0.176	0.065	
I'. AISI 4140		Reducing	0	0.060	0.130	0.050	0.110	0.040	- - -	0.028	0.005	51.68	9.34	18.00	0.225	0.048	
			15	0.080	0.020	0.040	0.970	0.200	- - -	0.025	0.007	53.00	14.06	5.30	0.426	0.037	
			25	0.060	0.020	0.040	0.950	0.220	- - -	0.026	0.006	51.20	14.37	5.00	0.267	0.036	
			70	0.385	1.030	0.400	1.150	0.230	- - -	0.021	0.010	35.38	22.28	2.30	0.116	0.016	
J. AISI 4140		Reducing	0	0.105	0.040	0.020	0.050	0.070	- - -	0.030	0.002	54.56	9.52	15.40	0.314	0.053	
			15	0.105	0.090	0.030	0.090	0.050	- - -	0.029	0.002	46.00	10.06	18.70	0.320	0.055	
			30	0.100	0.060	0.050	0.100	0.050	- - -	0.029	0.003	41.60	9.74	23.30	0.310	0.058	
			45	0.080	0.090	0.040	0.080	0.050	- - -	0.028	0.002	40.58	9.06	26.50	0.176	0.054	
			84	0.395	0.890	0.350	0.960	0.220	- - -	0.024	0.008	40.48	20.56	3.50	0.192	0.013	

*The symbols [i] and (i) denote the bulk weight percent of i in the metal and slag phases, respectively.

Consideration is first given to the dephosphorization or oxidizing period of the basic-electric heat. Rate data for this period in nine heats are presented in Table II. The least-squares technique was used to fit an equation of the form 14,

$$\log \frac{[P]}{[P]_0} = - \frac{a_P}{2.303} t, \quad \dots (16)$$

to the data of each heat. The resultant equations are graphed in Figure 1 and tabulated below.

$$A. \quad \log \frac{[P]}{[P]_0} = -0.00820t \quad \dots (17)$$

$$B. \quad \log \frac{[P]}{[P]_0} = -0.00397t \quad \dots (18)$$

$$C. \quad \log \frac{[P]}{[P]_0} = -0.00141t \quad \dots (19)$$

$$D. \quad \log \frac{[P]}{[P]_0} = -0.00490t \quad \dots (20)$$

$$E. \quad \log \frac{[P]}{[P]_0} = -0.00572t \quad \dots (21)$$

$$F. \quad \log \frac{[P]}{[P]_0} = -0.00219t \quad \dots (22)$$

$$G. \quad \log \frac{[P]}{[P]_0} = -0.00303t \quad \dots (23)$$

$$H. \quad \log \frac{[P]}{[P]_0} = -0.00202t \quad \dots (24)$$

$$I. \quad \log \frac{[P]}{[P]_0} = -0.00785t \quad \dots (25)$$

Correlation coefficients for the above relations are in the range -0.84 to -0.99. The Student's t test establishes the significance of the coefficients at the 0.05 confidence level.

Rate data for the desulfurization or reducing period of ten heats, eight of which correspond to heats wherein the oxidizing period is also treated in this report, are presented in Table III. A least-squares relation of the form

TABLE II
STEEL PHOSPHORUS LEVEL FROM MELTDOWN THRU THE OXIDIZING PERIOD

Heat	[P]	$\log \frac{[P]}{[P]_0}$	Elapsed Time (min)
A	0.022	0.000	0
	0.008	-0.439	20
	0.004	-0.740	80
	0.001	-1.347	150
B	0.012	0.000	0
	0.008	-0.176	30
	0.005	-0.380	85
	0.003	-0.602	145
C	0.009	0.000	0
	0.008	-0.051	20
	0.007	-0.109	80
	0.006	-0.176	115
D	0.008	0.000	0
	0.007	-0.058	20
	0.004	-0.301	80
	0.002	-0.602	120
E	0.011	0.000	0
	0.010	-0.041	20
	0.008	-0.138	80
	0.002	-0.740	110
F	0.009	0.000	0
	0.008	-0.051	20
	0.006	-0.176	80
	0.005	-0.255	115
G	0.017	0.000	0
	0.017	0.000	15
	0.016	-0.026	30
	0.015	-0.054	45
	0.015	-0.054	59
	0.011	-0.189	77
	0.009	-0.276	90
	0.009	-0.276	104
H	0.008	0.000	0
	0.008	0.000	15
	0.007	-0.058	30
	0.007	-0.058	45
	0.007	-0.058	60
	0.007	-0.058	75
	0.007	-0.058	90
	0.005	-0.204	105
	0.004	-0.301	120
I	0.011	0.000	0
	0.009	-0.087	20
	0.003	-0.564	80
	0.001	-1.041	135

TABLE III

STEEL SULFUR LEVEL FROM SHAPE-UP OF THE REDUCING
SLAG THRU THE REDUCING PERIOD

Heat	[s]	$\log \frac{[s]}{[s]_0}$	Elapsed Time (min)
A	0.029	0.000	0
	0.024	-0.082	10
	0.020	-0.161	20
	0.018	-0.207	50
	0.017	-0.232	66
B	0.033	0.000	0
	0.024	-0.138	16
	0.028	-0.072	31
	0.026	-0.103	46
	0.022	-0.176	68
	0.019	-0.240	79
C	0.018	0.000	0
	0.016	-0.051	15
	0.015	-0.079	30
	0.014	-0.109	45
	0.013	-0.112	61
D	0.014	0.000	0
	0.011	-0.105	15
	0.012	-0.067	25
	0.009	-0.192	40
	0.008	-0.243	55
	0.007	-0.301	70
	0.005	-0.447	104
E	0.018	0.000	0
	0.015	-0.079	15
	0.017	-0.025	30
	0.014	-0.109	45
	0.014	-0.109	60
	0.014	-0.109	75
	0.012	-0.176	90
F	0.017	0.000	0
	0.014	-0.084	11
	0.012	-0.151	26
	0.011	-0.189	41
	0.011	-0.189	56
	0.011	-0.189	71
	0.011	-0.189	86
	0.010	-0.231	101
	0.010	-0.231	101
G	0.021	0.000	0
	0.019	-0.043	20
	0.013	-0.208	44
	0.010	-0.322	59
	0.008	-0.419	74
	0.006	-0.544	94
	0.005	-0.623	101
	0.005	-0.623	101
H	0.022	0.000	0
	0.020	-0.041	10
	0.021	-0.020	14
	0.019	-0.063	29
	0.020	-0.041	40
	0.020	-0.041	53
	0.018	-0.087	57
	0.016	-0.138	62
	0.015	-0.166	77
	0.016	-0.138	82
	0.015	-0.166	111
	0.015	-0.166	111
	0.015	-0.166	111
I'	0.028	0.000	0
	0.025	-0.049	15
	0.026	-0.032	25
	0.021	-0.125	70
J	0.030	0.000	0
	0.029	-0.015	15
	0.029	-0.015	30
	0.028	-0.030	45
	0.024	-0.097	84

$$\log \frac{[S]}{[S]_0} = -\frac{a_s}{2.303} t \quad \dots (26)$$

was obtained for each set of data. These are graphed in Figure 2 and tabulated below.

$$A. \quad \log \frac{[S]}{[S]_0} = -0.00319t \quad \dots (27)$$

$$B. \quad \log \frac{[S]}{[S]_0} = -0.00241t \quad \dots (28)$$

$$C. \quad \log \frac{[S]}{[S]_0} = -0.00185t \quad \dots (29)$$

$$D. \quad \log \frac{[S]}{[S]_0} = -0.00424t \quad \dots (30)$$

$$E. \quad \log \frac{[S]}{[S]_0} = -0.00160t \quad \dots (31)$$

$$F. \quad \log \frac{[S]}{[S]_0} = -0.00180t \quad \dots (32)$$

$$G. \quad \log \frac{[S]}{[S]_0} = -0.00634t \quad \dots (33)$$

$$H. \quad \log \frac{[S]}{[S]_0} = -0.00155t \quad \dots (34)$$

$$I. \quad \log \frac{[S]}{[S]_0} = -0.00170t \quad \dots (35)$$

$$J. \quad \log \frac{[S]}{[S]_0} = -0.00113t \quad \dots (36)$$

Correlation coefficients for the above relations are in the range -0.86 to -0.99. The Student's t test establishes the significance of the coefficients at the 0.05 level.

Consequences of the use of the total mass percent of the element (combined or free) in Equation 14 in place of the mass percent of the transferring species and the implicit assumption of a single transferring species are considered later.

From Equations 17 through 25 and 27 through 36, the ratio of the diffusion coefficient to the effective boundary layer thickness for the transferring species was calculated in each case using Equation 10.

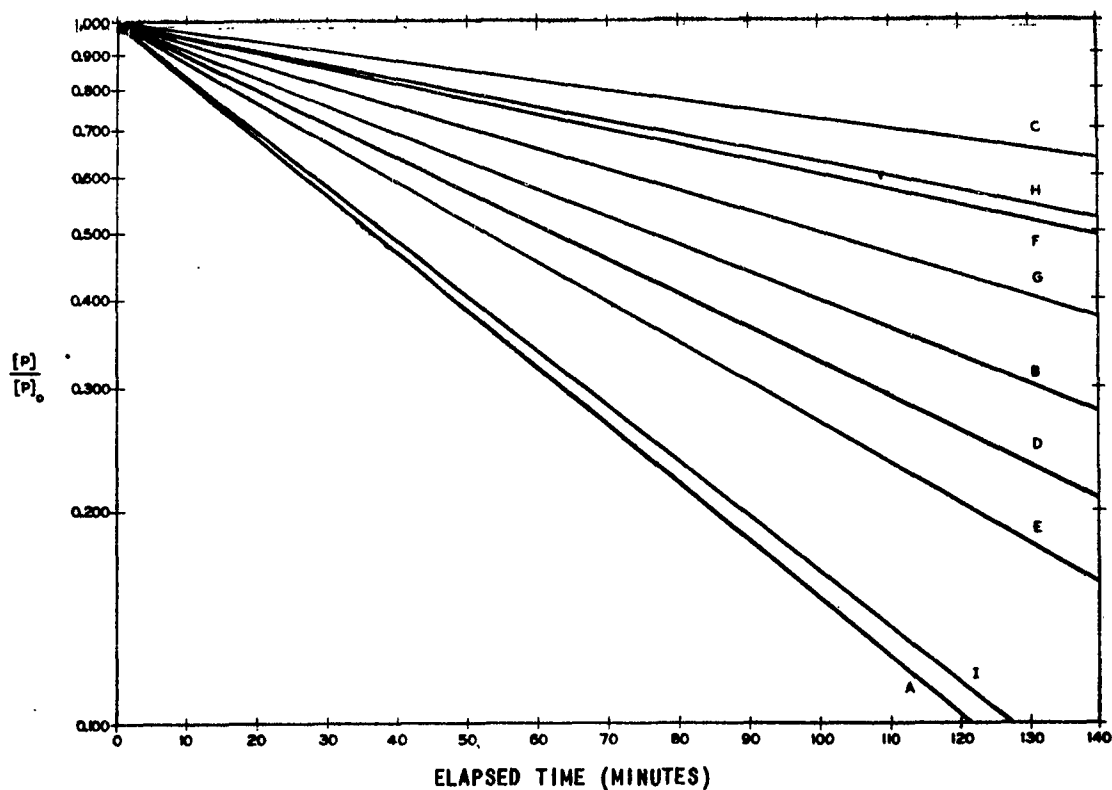


FIGURE 1: VARIATION OF $\frac{[P]}{[P]_0}$ WITH PROCESS TIME IN THE OXIDIZING PERIOD

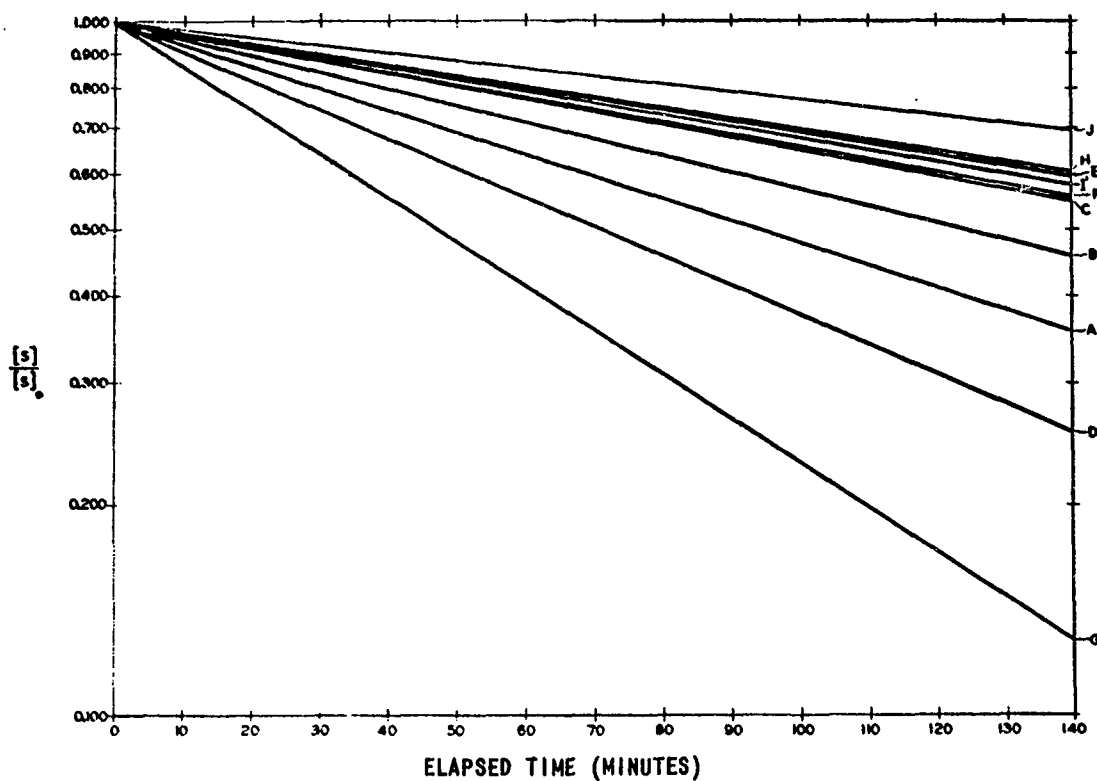


FIGURE 2: VARIATION OF $\frac{[S]}{[S]_0}$ WITH PROCESS TIME IN THE REDUCING PERIOD

The volume of the metal phase was computed on the basis of the charged mass of metal and an appropriate density. The area of metal-slag contact was computed assuming a spherical hearth. The results are tabulated in Table IV.

TABLE IV
CALCULATED VALUES OF THE RATIO D_i/δ_i

Heat	a_p (min) ⁻¹	A/V (cm) ⁻¹	D_p/δ_p (cm)(min) ⁻¹	a_s (min) ⁻¹	A/V (cm) ⁻¹	D_s/δ_s (cm)(min) ⁻¹
A	0.01888	0.05206	0.3627,	0.00735	0.05206	0.1412
B	0.00914	0.05380	0.1699	0.00555	0.05380	0.1032
C	0.00325	0.05206	0.0624	0.00426	0.05206	0.0818
D	0.01128	0.04863	0.2320	0.00976	0.04863	0.2007
E	0.01317	0.04870	0.2704	0.00368	0.04870	0.0756
F	0.00504	0.04746	0.1062	0.00415	0.04746	0.0874
G	0.00698	0.04666	0.1496	0.01460	0.04666	0.3129
H	0.00465	0.04666	0.0997	0.00357	0.04666	0.0765
I	0.01808	0.04784	0.3779	- - - -	- - - -	- - - -
I'	- - - -	- - - -	- - - -	0.00392	0.05094	0.0770
J	- - - -	- - - -	- - - -	0.00260	0.05206	0.0499

Correlation of Metal and Slag Composition with Refining Process Rate

The evident variation of the slopes of the lines shown in Figures 1 and 2 requires consideration. Variation of these slopes or, more precisely, variation of the general terms a_i , as defined by Equation 10, can be attributed to variation of A/V and/or D_i/δ_i . Unintentional variation of the A/V term proves of no theoretical interest; separation of this term from each a_i shows yet a variation of the remaining term D_i/δ_i (Table IV). While possible causes for this variation are numerous, chemistry alone will be considered here. Some basis for this approach lies in the minor variation of the system size and shape and the constancy of other factors which control the convection conditions. Furthermore, procedure must necessarily be along empirical lines.

The importance of the role played by the chemistry of both metal and slag phases on the processes of phosphorus and sulfur removal from iron base alloys has been made clear by previous works.^{8,9} It has been shown that low alloy content, high metal and slag oxygen level, and sufficiently high slag basicity $[(CaO)/(SiO_2)]$ are necessary conditions for effecting phosphorus removal. Conversely high alloy content, low metal and slag oxygen level, and sufficiently high slag basicity are necessary conditions for effecting sulfur removal. These conclusions

are based on extensive thermodynamic considerations and experimental findings. Also, it is recognized that the composition of a phase determines, in part, the diffusion coefficient of species within the phase. Further, it is entirely within reason to postulate that composition affects (directly or indirectly) the effective boundary layer thickness of a transferring species. For example, agitation of the metal both by evolution of gaseous oxides (of carbon in particular) during the oxidizing period (the degree of which is influenced by composition) undoubtedly affects the value of the boundary layer thickness for a transferring species in a manner analogous to forced convection. Hence, sufficient motivation exists for attempting to establish a relation connecting the mass transfer coefficient D_i/δ_i with chemistry. A discussion of the composition variables appearing in such a relation is necessary. Use of instantaneous values leads to some difficulty. Indeed, this procedure contradicts a previous assumption (assumption of constant a_i in Equation 9), one which is not invalidated by the results, Equations 17 through 25 and 27 through 36. Thus the concept of a "characteristic composition" is employed; and a single set of composition numbers is used to characterize an entire processing period. Convenient compositions include the initial composition (that at the start of an observation period) and the average composition.* Use of average values is the more logical choice; however, initial values are of greater utility for prediction purposes. Both are employed. The selection of elements and/or compounds to be included in the analysis is made on the basis of past observation as to considered importance in aiding or deterring removal of the element in question. Also, the analysis is made within bounds of available data.

The least-squares technique was used to construct first-approximation relations of the form

$$\frac{D_i}{\delta_i} = \sum_{k=1}^n c_k x_k + b, \quad \dots (37)$$

where the x_k are the selected composition variables and the c_k and b are constants. Two relations of the form 37 were obtained for each of the two periods, one utilizing initial values of the n variables and the other average values. These relations are shown below.

$$\begin{aligned} \frac{D_P}{\delta_P} = & 2.1323 - 1.2431 [C]_0 - 1.9532 [Mn]_0 + 0.7616 [Si]_0 + 0.1996 [Cr]_0 \\ & - 0.0391 (FeO)_0 - 0.1016 \frac{(CaO)_0}{(SiO_2)_0} \quad \dots (38) \end{aligned}$$

*The average value of the function $[i] = \Psi(t)$ in the closed interval $0 \leq t \leq t'$ is defined by the integral $[\bar{i}] = \frac{1}{t'} \int_0^{t'} [i] dt$.

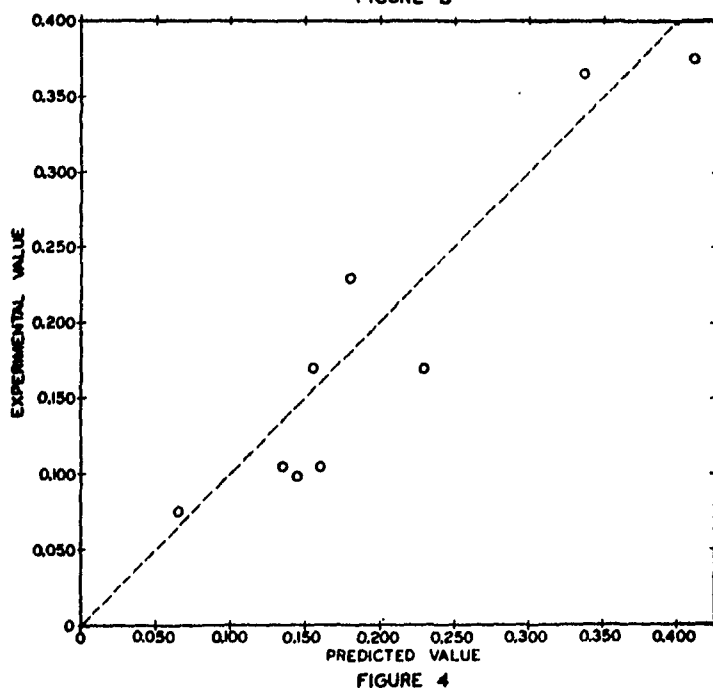
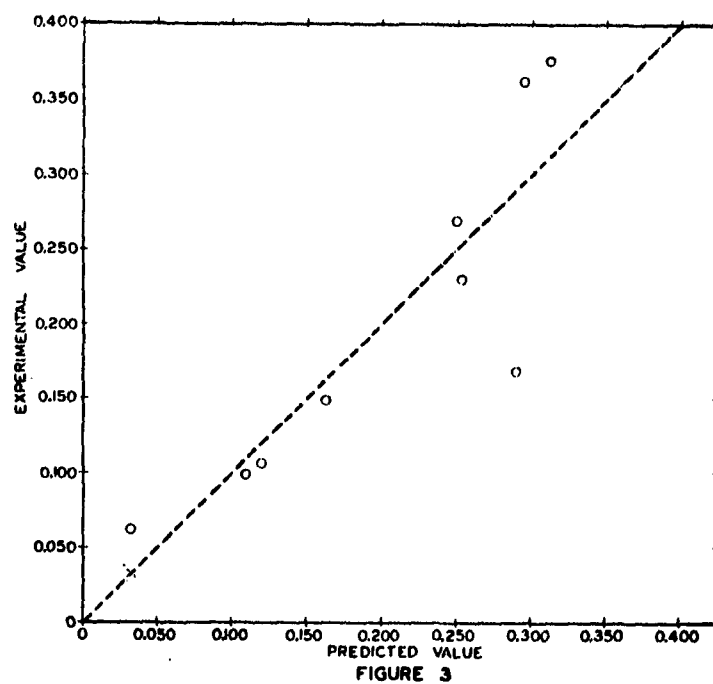
$$\frac{D_P}{\delta_P} = 1.3139 [\bar{C}] - 1.2239 [\bar{C}] - 3.2964 [\bar{Mn}] - 12.0355 [\bar{Si}] - 0.6490 [\bar{Cr}] \\ - 0.1805 (\bar{FeO}) + 2.0703 \frac{(\bar{CaO})}{(\bar{SiO}_2)} \quad \dots (39)$$

$$\frac{D_S}{\delta_S} = -0.0268 + 0.5521 [C]_o - 0.6366 [Mn]_o + 1.4197 [Si]_o + 0.1348 [Cr]_o \\ + 0.0739 \frac{(CaO)_o}{(SiO_2)_o(FeO)_o} \quad \dots (40)$$

$$\frac{D_S}{\delta_S} = 0.0430 + 0.0311 [\bar{C}] - 0.1915 [\bar{Mn}] + 0.4018 [\bar{Si}] + 0.0009 [\bar{Cr}] \\ + 0.1182 \frac{(\bar{CaO})}{(\bar{SiO}_2)(\bar{FeO})} \quad \dots (41)$$

The slag-defining variables appearing in Equations 38 and 39 are lumped into a single parameter in 40 and 41. The relations 38 through 41 are the results of many trials utilizing the form 37 with various selections of the variables x_k (initial and average values); they are judged "best" of all trials by means of the multiple correlation coefficient. Multiple correlation coefficients for Equations 38, 39, 40, and 41 are 0.869, 0.943, 0.929, and 0.979, respectively. The Student's t test establishes the significance of the coefficients at the 0.01 confidence level in the case of Equation 38 and at the 0.001 confidence level in the case of 39, 40, and 41. In Figures 3 and 4 the experimental values of D_P/δ_P (values in Table IV) are compared with values obtained from Equations 38 and 39, respectively. In Figures 5 and 6 the experimental values of D_S/δ_S (values in Table IV) are compared with values obtained from Equations 40 and 41, respectively.

Existing views hold that low alloy levels of carbon, manganese, silicon, and chromium together with high slag iron oxide content and high slag basicity aid in phosphorus removal. Equation 38 does little to strengthen these views, while 39 (the "better" of the two relations) shows excellent agreement with accepted views in that all coefficients, save the coefficient of the iron oxide term, display the proper sign. Similarly, views are held that high alloy levels of carbon, manganese, silicon, and chromium and high levels of the slag-defining parameter $[(CaO)/(SiO_2)(FeO)]$ aid in sulfur removal. Here, both Equations 40 and 41 agree with accepted views in that, but for the coefficient of the manganese term, the coefficient of all terms has the proper sign. Also strengthened is the concept of the two-slag refining process,⁷ a summary of which is included



COMPARISON OF EXPERIMENTAL AND PREDICTED
VALUES OF D_p/δ_p

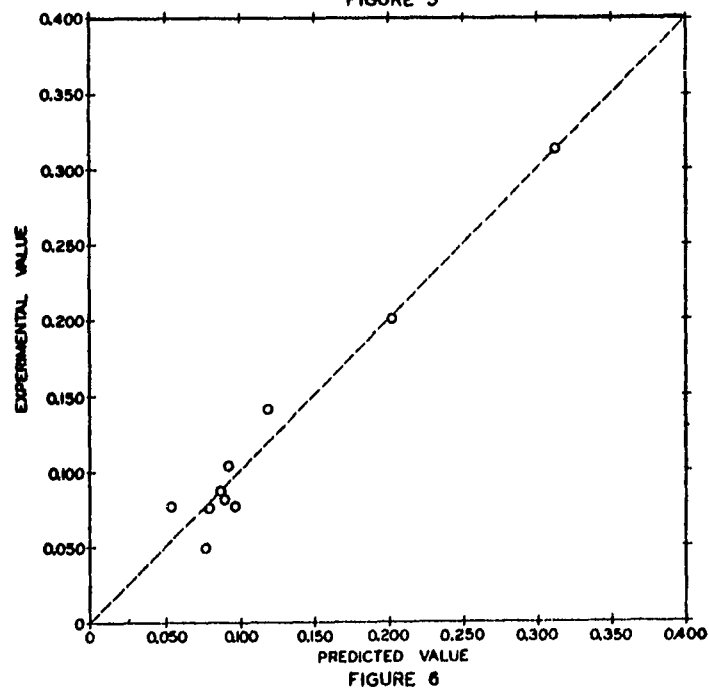
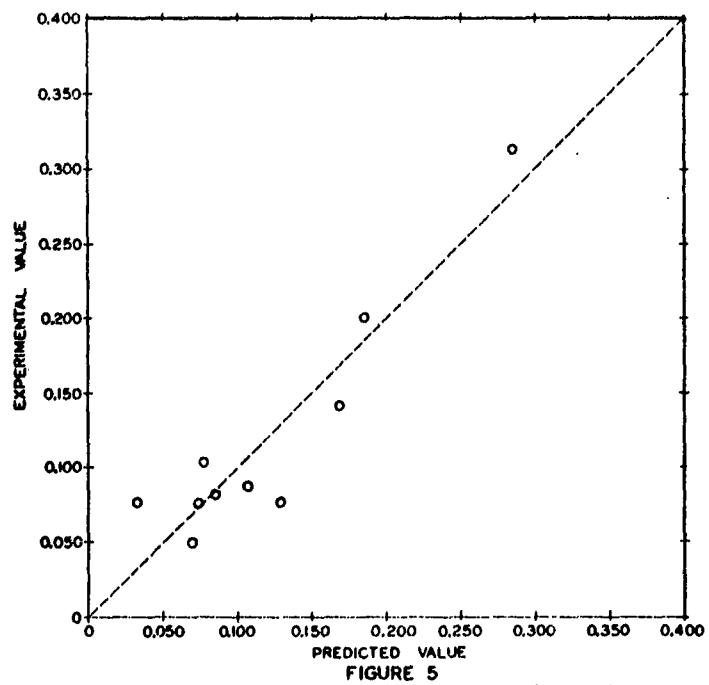


FIGURE 5
FIGURE 6
COMPARISON OF EXPERIMENTAL AND PREDICTED
VALUES OF D_s/δ_s

here for completeness. Optimum practice for phosphorus and sulfur removal is realized utilizing two periods in the following sequence:

1. An oxidizing period using a low alloy melting stock and a highly oxidizing basic slag for maximum dephosphorization.
2. A reducing period using a fresh, low oxidizing basic slag and a re-alloyed steel bath (not to exceed aim analysis) for maximum desulfurization.

The necessity of such a practice is made clear, in part by the opposite effect of the elemental content on the terms D_p/δ_p and D_s/δ_s . Hence, the relations 39 through 41 may be said to constitute a formal (kinetic) basis for several of the conclusions reached in previous investigations.

In the development and application of the kinetic model, Equation 14, it is conveniently assumed that the element removed from the metal during the refining process exists in a single form - the transferring species. The level of this one species is taken as the level of the element. Justification of the latter point is now made. The mass percent of an element is related to the mass percent of a single element-bearing molecular species by the equation

$$Z_j = p_i \left[\frac{(AW)_j}{(MW)_i} \right] Z_i, \quad \dots (42)$$

where the subscript j is reserved for an elemental species, the subscript i refers to the species containing j , p denotes the number of atoms of j in a molecule of i , AW denotes atomic weight, and, as before, Z and MW denote mass percent and molecular weight, respectively. Equation 42 can be written in the form

$$\ln Z_j = \ln \left[p_i \frac{(AW)_j}{(MW)_i} \right] + \ln Z_i, \quad \dots (43)$$

and this result differentiated to give

$$d \ln Z_j = d \ln Z_i. \quad \dots (44)$$

Equation 44 permits the use of elemental mass percent in Equation 14.

The hypothesis of a single transferring species allows only minor variation in the term D_i/δ_i with composition. The extreme variation of D_s/δ_s and D_p/δ_p with process period (essentially a variation of same with chemistry) is not consistent with the hypothesis. Further inconsistency lies in the observation that although the instantaneous composition during

each oxidizing period varies widely, linear plots result from the use of Equation 16, the derivation of which assumes a constant D_p/δ_p , and yet the D_p/δ_p obtained varies with the process period. Hence, the concept of a characteristic composition (initial and/or average) which determines the value of D_i/δ_i suggests itself. This is the basis for Equations 38 through 41; and while some reasoning has been presented to explain these results, the following is put forward as a more plausible interpretation.

A more realistic approach than that previously taken is to envision m transferring species in a period. Let each species transfer in accordance with Equation 9. The number of atomic weights of element j present in the metal phase at any time t is

$$N_j = \sum_{i=1}^m p_i N_i. \quad \dots (45)$$

Notation conforms with that previously defined. Division of both sides of Equation 45 by V and differentiation of the resulting equation yields

$$\frac{dC_j^B}{dt} = \sum_{i=1}^m p_i \frac{dC_i^B}{dt}, \quad \dots (46)$$

from which, by introduction of Equation 9, there follows

$$-\frac{dC_j^B}{dt} = \left(\sum_{i=1}^m p_i C_i^B \frac{D_i}{\delta_i} \right) \frac{A}{V}. \quad \dots (47)$$

The fraction of atomic weights of j contained in i is defined as

$$\alpha_i = \frac{p_i C_i^B}{C_j^B}. \quad \dots (48)$$

From Equations 47 and 48 there is obtained

$$-\frac{dC_j^B}{dt} = \left(\sum_{i=1}^m \alpha_i \frac{D_i}{\delta_i} \right) \left(\frac{A}{V} \right) C_j^B. \quad \dots (49)$$

Passage from Equation 49 to a similar equation in which C_j^B is replaced by Z_j , the mass percent of element j contained in all species, is made in the same way as the transition from Equation 9 to Equation 13. While integration of Equation 13 is permissible for no variation in a_i with time, integration of Equation 49, for $m > 1$, is not possible under the analogous assumption of constancy of the $m a_i$ in Equation 49 over the process period. Hence an analysis using Equation 13 as a model (Equation 49 with $m=1$) will show discrepancy (deviation of experimental data from Equation 14) if the correct model is in fact Equation 49 with $m > 1$. If the deviation is not pronounced (little or no variation in $\sum_{i=1}^m a_i (D_i/\delta_i)$)

with time allowing the integration of Equation 49 to the form of 14), the model, Equation 13, is acceptable. However extreme variation in the term D_i/δ_i of Equation 14 with a characteristic composition is obvious, a priori, since it is now to be interpreted as equal to $\sum_{i=1}^m a_i (D_i/\delta_i)$.

The concept of the single transferring species is not to be rejected, however; the term D_i/δ_i of Equation 14 is to be interpreted, instead, as an effective ratio whose variation with "composition" must be determined.

The Matter of Extrapolation

While positive statements concerning the extension of the Equations 38 through 41 to geometrically similar systems of greater or lesser capacity cannot be made here, the following development illustrates the approximations involved in any attempt at extrapolation of these results.

It is known that for mass transfer under conditions of forced convection a relation of the form

$$Nu = f_1 (Re, Sc) \quad \dots (50)$$

exists; for mass transfer under conditions of free convection a relation of the form

$$Nu = f_2 (Gr, Sc) \quad \dots (51)$$

exists.¹⁰ Here Nu is the Nusselt number, Re is the Reynolds number, Sc is the Schmidt number, and Gr is the Grashof number. Definitions of these dimensionless quantities follow:

$$Nu \equiv \frac{x}{\delta}, \quad Re \equiv \frac{x u \rho}{\mu}, \quad Sc \equiv \frac{\mu}{D \rho}, \quad \text{and} \quad Gr \equiv \frac{g x^3 \rho^2}{\mu^2} \left(\frac{\gamma_B}{\gamma_P} - 1 \right), \quad \dots (52a, b, c, d)$$

where x is a characteristic dimension; δ and D are the effective boundary

layer thickness and diffusion coefficient for the transferring species; u , ρ , μ , and γ_B are the fluid bulk flow velocity, density, viscosity, and specific weight, respectively; γ_p is the specific weight of the fluid at the fluid boundary; and g is the gravitational constant.

Mass transfer in the metal bath during the oxidizing period is assumed to approximate that under conditions of forced convection. It is further assumed that the only variable affecting the velocity distribution is the system capacity, characterized by x . A convenient form of Equation 50, used extensively in former works, is

$$Nu = cRe^a Sc^b, \quad \dots (53)$$

where c , a , and b are constants, determined empirically. Assuming a relation of the form 53,

$$\left(\frac{x}{\delta}\right) = c \left(\frac{xu\rho}{\mu}\right)^a \left(\frac{\mu}{D\rho}\right)^b, \quad \dots (54)$$

in the present case and solving for δ yields

$$\delta = \frac{1}{c} x^{1-a} u^{-a} \rho^{b-a} \mu^{a-b} D^b. \quad \dots (55)$$

Denote by subscript 1 the system under study and by subscript 2 a similar system of greater or lesser capacity. Now

$$\delta_1 = \frac{1}{c} x_1^{1-a} u_1^{-a} \rho_1^{b-a} \mu_1^{a-b} D_1^b, \quad \dots (56a)$$

and

$$\delta_2 = \frac{1}{c} x_2^{1-a} u_2^{-a} \rho_2^{b-a} \mu_2^{a-b} D_2^b. \quad \dots (56b)$$

Division of Equation 56a by Equation 56b and use of the similarity condition yields

$$\left(\frac{\delta_1}{\delta_2}\right) = \left(\frac{x_1}{x_2}\right)^{1-a} \left(\frac{u_1}{u_2}\right)^{-a} \quad \dots (57)$$

The assumptions to this point have been somewhat realistic. However, in order to neglect variation in δ with size of the reaction vessel, procedure must be made under the poor assumptions of equal velocity distributions and a value of the exponent, a , sufficiently close to unity. In the absence of sufficient data, no alternatives exist; and the "scale" effect must be overlooked in extrapolation of the Equations 38 and 39. It may be in order to note here the results contained in Reference 1 illustrating the weak sensitivity of sulfur transfer rate to mechanical stirring.

Mass transfer in the metal bath during the reducing period is assumed to approximate that under conditions of free convection. Taking the form of Equation 51 as

$$Nu = k Gr^e Sc^f, \quad \dots (58)$$

where k , e , and f are empirical constants, and proceeding as before leads to the result

$$\left(\frac{\delta_1}{\delta_2}\right) = \left(\frac{x_1}{x_2}\right)^{1-3e} \quad \dots (59)$$

Neglect of the "scale" effect in this case is permissible when e is sufficiently close to $1/3$. Procedure must be made under this assumption if Equations 40 and 41 are to be extrapolated to vessels of capacity other than 6-1/2 tons.

Note on Minimization of Process Time

A consideration of minimization of the process time for removal of i follows. The discussion focuses on Equations 9 (single species hypothesis) and 49 (case of several transferring species). Obviously, in either case, conditions which result in a maximum value for the term(s) a_i are desired. This term is separated into its components, D_i/δ_i and A/V ; the A/V component is considered later. For an ideal system consisting of a single transferring species (transferring in accordance with Equation 9 and chemistry playing no kinetic role), maximization of D_i/δ_i is realized at the highest permissible operating temperature as set by materials of construction and with the metal bath in a well-stirred condition. For real systems, however, in which chemistry plays the major kinetic role, certain operating procedures dictated by the model are altered or omitted entirely because of the overriding effects of composition. Hence, for example, the bath temperature is maintained at its highest permissible level (2950 F) during the reducing period but is at a lower level (2850 F) during the oxidizing period because of the known adverse effect of high temperature on dephosphorization. For real systems, then, relations such as Equations 38 through 41 must be employed (within their range of applicability) in establishing optimum chemistry and practice.

A maximum value for A/V is optimum for either model, Equation 9 or 49. It is assumed that the value of this term is fixed in any given process period. The idealistic representation of the reaction vessel employed (furnace hearth taken as spherical) is shown in Figure 7. The ratio of the metal slag contact area to the metal volume is approximated

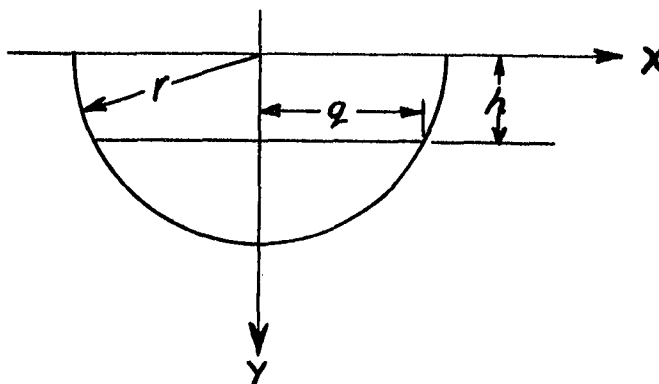


FIGURE 7: MODEL REACTION VESSEL

by the ratio of the area of the circle $x^2 + z^2 = q^2$ to the volume bounded by sphere $x^2 + y^2 + z^2 = r^2$ and the planes $y = h$ and $y = r$; or

$$\frac{A}{V} = \frac{r^2 - h^2}{\frac{2}{3} r^3 - hr^2 + \frac{1}{3} h^3} \quad \dots (60)$$

For fixed r , A/V is a function only of h . It can be shown that this function is monotone-increasing with h in the range $0 \leq h < r$ and so attains a maximum for $h \rightarrow r$. It is evident, then, that processing conditions must necessarily fall short of optimum.

A consideration of minimization of process operating cost would undoubtedly influence the reported observations. Such a consideration is, however, beyond the scope of this work, although it is to this end that the effort made herein is directed.

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